

OIL SHALE RETORTING PROCESSES: A TECHNICAL OVERVIEW

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This paper was prepared for publication in
Proceedings of the 17th Oil Shale Symposium,
Golden, Colorado, April 16-18, 1984.

March 1984

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OIL SHALE RETORTING PROCESSES: A TECHNICAL OVERVIEW

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ABSTRACT

The challenge facing the oil shale industry is to devise a simple and efficient retorting process that operates at low cost. This will require a thorough understanding of the important physical and chemical processes that occur during retorting, mathematical modeling to analyze the complex interactions, and sophisticated engineering to design a retorting process having the minimum cost.

Retorting processes can be classified into two groups, one using hot gas as the heat transfer medium and one using hot solid material. We have constructed mathematical models of two generic processes from each of these groups to represent state-of-the-art processes as well as those under development. The models are based on detailed reaction kinetics, thermodynamics, and process physics. Using these models, we have calculated the process characteristics and the complete mass and energy balances for 50,000-barrel/day shale oil plants.

We have made comparisons of these four processes to illustrate their advantages and disadvantages. The comparisons include retort vessel volume, heat exchange capacity, power requirements, water requirements, and waste gas volume. The results indicate no present easy choice of a best process. Oil shale process technology is neither highly developed nor mature, and substantial improvements can be expected from further research and development, and from industrial experience. The hot gas processes can be viewed as first-generation technology, and the hot solid processes, if they can be successfully developed, may be second-generation technology.

INTRODUCTION

The United States has vast quantities of oil shale, enough to supply our liquid fuel needs for centuries. Oil can be obtained by simply heating the shale to convert the organic material it contains to shale oil. The technical challenge is to do this at a cost that makes the shale oil competitive with conventional petroleum. Historically, in several other coun-

tries shale oil competed successfully with petroleum in the early days of the petroleum industry. Yet in recent times no one has demonstrated a shale oil process that is economically competitive as measured against current world costs of petroleum.

Experience with present oil-shale retorting processes varies in scale from small laboratory experiments to larger pilot and semi-works plants processing as much as a few hundred tons per day. Union Oil Company is expected to begin production soon in its new 10,000-barrel/day plant in Colorado. Development in this industry is at an early stage, and we believe there is substantial room for technical improvements with accompanying reductions in cost. Progress may be expected both in the improvement of present processes and in the development of new processes.

PYROLYSIS AND OXIDATION OF OIL SHALE

Our important oil shale reserves are in the Green River formation in the western United States. This oil shale is an impure marlstone consisting mostly of inorganic mineral matter. In a typical shale the solid organic constituent, kerogen, comprises some 15% of the rock by mass and 30% by volume. The rock is so fine grained (see Fig. 1) as to preclude any process for grinding it into particles to physically separate the kerogen from the mineral matter. Liquid extraction processes are likewise inapplicable, for the raw shale is essentially impermeable to fluids, and the kerogen is not soluble.

Retorting of oil shale to produce shale oil requires that the shale be broken into pieces small enough for good heat transfer and heated to about 500°C. The kerogen decomposes or pyrolyzes rapidly at this temperature, evolving oil vapor and gas, and leaving behind solid char. The amounts, compositions, and energy resulting from combustion of the various components produced by the pyrolysis of kerogen^{1,2} are shown in Fig. 2.

Heat for the retorting process is provided most efficiently by burning some of the products of pyrolysis--preferably the less valuable products. The oil

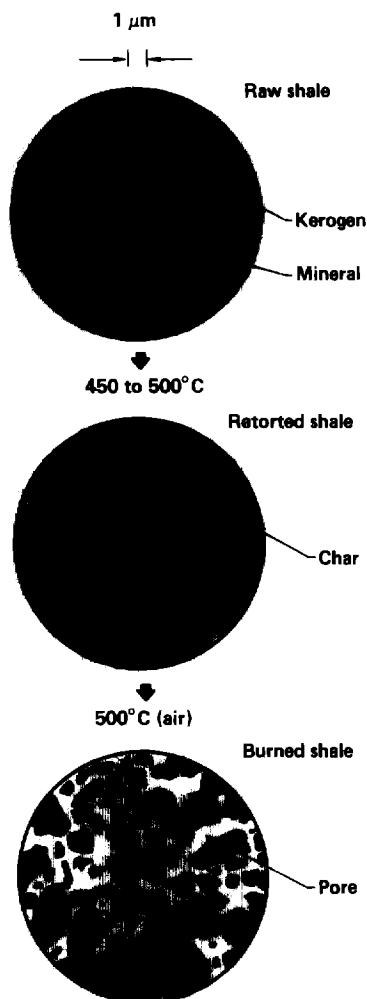


Fig. 1. Microstructure of oil shale, showing the physical relationship between the organic (kerogen) and inorganic (mineral) components.

is the most valuable product, and the gas is potentially valuable as a source of hydrogen for upgrading shale oil or as a source of marketable gas. Char is the least valuable product, and hence it is the fuel of choice for providing process heat. Unfortunately, not all processes permit a choice of fuel.

In addition, in most processes the mineral matter in the shale is not inert. The carbonate minerals dolomite and calcite are major components of these shales, and the dolomite especially is subject to decomposition at temperatures and times typical of combustion processes.³ Reactions between mineral matter and gases are also important, both in the reducing conditions typical of pyrolysis and in the oxidizing conditions typical of the combustion portion of the processes.⁴ Participation of the mineral solids in the

process is unwelcome when it requires a large amount of energy, as in the case of carbonate decomposition, but welcome when it removes sulfur-containing gases from the gas stream, thus reducing or eliminating a source of air pollution.

Some of the oil produced may be destroyed, within the processing cycle, before it is recovered.⁵ For example, oil in the vapor phase will crack if subjected to high temperature, producing mostly lighter gaseous hydrocarbons (exposure to 550°C for only 2 seconds will result in a loss of about 10% of the oil). Oil in the liquid phase will coke at elevated temperature, producing mostly solid hydrocarbon products; fortunately, the loss in oil yield from this mechanism is insignificant at the rapid heating rates characteristic of aboveground retorting processes. In addition, oil and oil vapor can be destroyed by burning if they are exposed to oxidizing conditions during the retorting process.

The technical challenge, then, is to devise a simple and efficient oil-shale retorting process that operates at low cost. This will require an accurate and thorough understanding of the important physical and chemical processes that occur during retorting and of their interactions in a complex system, mathematical modeling to obtain the necessary information logically and efficiently (rather than by trial-and-error experimentation), and sophisticated engineering to design a retorting process that can be built and operated at minimum cost.

DIFFERENT RETORTING PROCESSES

Many different processes have been proposed for retorting oil shale. For the most part they have evolved from different methods for heating solid particles (in this case, oil shale particles). Either hot gas or hot solid material may be used to supply heat to the shale. Hot liquids are not practical for temperatures near 500°C.

The classification of processes described below is a useful means of identifying and evaluating the many processes that can be considered for retorting oil shale. The processes referred to by company name are simply convenient examples that illustrate the generic process types. Many other process variations are possible within each class described, and other processes exist which are not listed as examples.

Heat Transfer from Hot Gas

If hot gas is chosen as the heat transfer medium, the broken-up shale is distributed in a packed bed

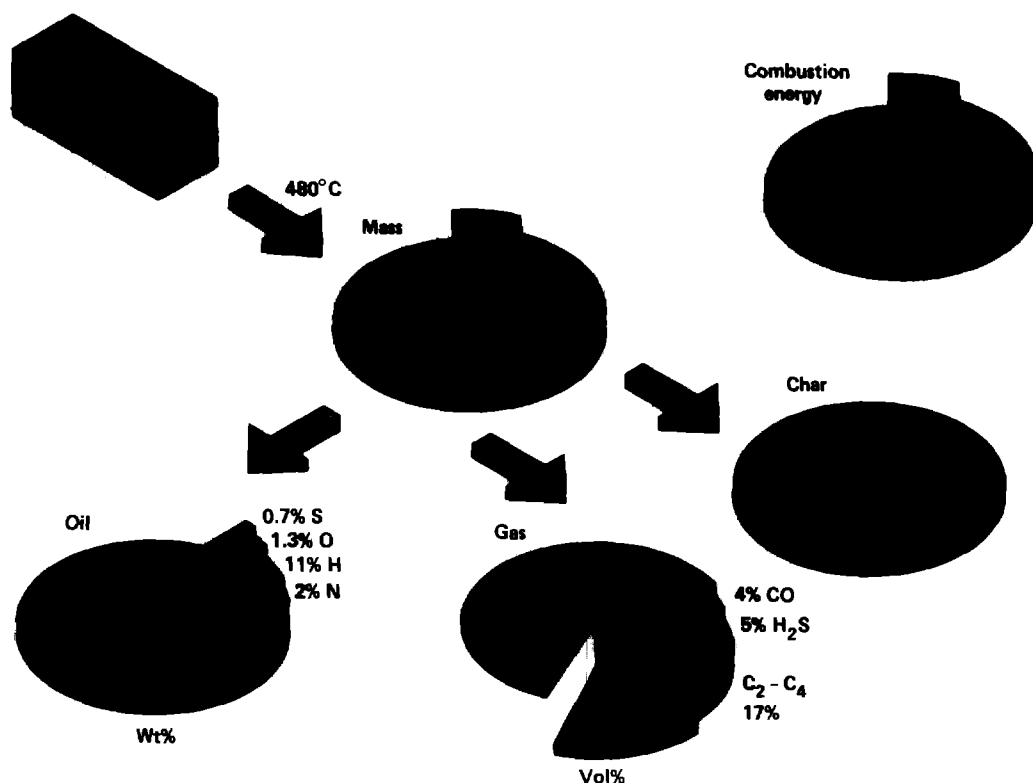


Fig. 2. Typical decomposition products from kerogen. When heated, kerogen decomposes into the mass fractions of oil, gas, and char shown; the chemical composition of each is indicated. The percent combustion energy obtained by burning each component is also given.

through which hot gas is pumped to heat the shale particles. The various types of hot gas retorts have certain characteristics in common. For instance, the mass of gas required to process a unit mass of shale ranges from 0.6 to 0.8, a ratio that derives from the relative heat capacities of the shale and the gas. As a result, large volumes of gas are required, and the resistance of the bed to the flow of gas must be minimized to avoid large gas-pumping costs.

Fine particles are undesirable in packed beds because they restrict the gas flow or increase the pressure drop across the bed. Therefore particles of shale less than about 0.5 cm in diameter must be discarded or processed in some other way. Large particles, on the other hand, require a relatively long time to heat, which adds to the cost by increasing the residence time of shale in expensive equipment and by loss of oil through coking, which occurs if the heating is very slow. The maximum practical size limit for shale particles in hot gas retorts is probably a diameter between 5 and 10 cm.

Table 1 lists the various kinds of hot gas retorts. Packed shale beds may be either fixed or

moving. The gas may be heated either internally by combustion of fuel within the retort (direct) or externally in some kind of heater (indirect). Brief descriptions of the hot gas retorts listed in Table 1 follow:

- In the Paraho internal combustion retort,⁶ a moving bed of shale travels downward and is heated by hot gas flowing upward through it. The hot gas is provided by combustion of hydrocarbon gas and char within the retort. Oil produced from the pyrolysis process is carried out of the retort by the gas stream, in the form of vapor and oil mist (liquid).

Table 1. Classification of hot gas processes for retorting oil shale. Hot gas is passed through a packed bed of shale particles to heat and retort the shale.

Packed-bed retorts		Gas heater type
Fixed bed	Moving bed	
MIS	Paraho	Internal combustion (direct)
NTU	Union B	
Superior	Union B	External combustion (indirect)
	Petrosix	

● In both the Union B⁷ and the Petrosix⁸ retorts, the hot gas is provided by heating the hydrocarbon gases produced by pyrolysis in an external heater. The hot gas flows counter to the flow of shale particles. In the Union B process the shale is pumped upward and the gas flows downward, whereas in the Petrosix process the shale flows downward and the gas flows upward. Fuel from an external source must be supplied to operate the heater.

● The NTU process⁹ is a batch process. Oil shale is dumped into a retort, heated by hot gas produced by combustion of hydrocarbons within the retort, and then removed. Processes similar to this have been used in the past and are still used or considered where a simple though inefficient process is acceptable.

● The Superior process¹⁰ is a hybrid in some ways. Shale is loaded onto a moving circular grate to form a fixed bed which is carried through a hot-gas retorting zone, with the hot gas supplied by an external heater. The fixed bed is then carried through an oxidizing zone where some heat is produced by combustion of char and used to preheat gas.

● In the modified in situ (MIS) process,¹¹⁻¹³ a fixed-bed retort is constructed underground by some combination of mining and blasting. Downward-flowing hot gas is provided by combustion of char in the retort. Because of the method of construction, little control over particle size is possible, and the bed contains particles less than 0.5 cm in diameter as well as particles larger than 10 cm in diameter. As a result, the retorting rate is slow and oil yield is reduced. Another serious problem is the difficulty in obtaining uniform permeability, which reduces the fraction of the bed that is swept by the retorting front.

Heat Transfer from Hot Solid

If hot solid material is chosen as the heat transfer medium, the various processes may be classified on the basis of the method of mixing the solid with the raw shale and the method of heating the solid (Table 2). The heat transfer from hot solid to raw shale depends mainly on the convection of the gas that is present and only to a small extent on conduction and radiation. The oil vapor and gases produced during pyrolysis play a significant role in the heat transfer. In all these hot-solid processes, the raw shale is crushed to a size small enough for rapid heat transfer. Either shale itself (after being retorted) or another solid may be used for the heat transfer medium. When retorted shale particles are used as the heat-carrying solid (they are heated by burning the char that remains on them after retorting), the need to separate two solids is avoided by using more hot retorted shale than raw shale and then discarding the excess solid somewhere in the process. If another solid is used (e.g., ceramic balls), it must be easily separated from the shale. In these processes, large solids are separated from fine shale by screening and are reheated in a packed bed or ball heater of some kind, with hot gas used as the heat transfer agent.

Brief descriptions of the hot solid processes listed in Table 2 are given below:

● In the Tosco II process,¹⁴ hot ceramic balls are mixed with smaller shale particles in a rotating drum. After the shale is pyrolyzed, the balls are separated from it and reheated in a ball heater using gas as fuel. The retorted shale is discarded.

● In the Shell SPHER process,¹⁵ hot balls fall through a fluidized bed of small shale particles. The balls are then separated from the shale and reheated

Table 2. Classification of hot solid processes for retorting oil shale. Hot solid particles are mixed with shale particles to heat and retort the shale.

<u>Stirred-bed retorts</u>		<u>Solid heater type</u>
<u>Mechanical mixing</u>	<u>Fluidized bed</u>	
Tosco II (drum mixing)	Shell SPHER (gas mixing)	Packed bed, large solid particles, gas fuel
Lurgi (screw mixing) LLNL (gravity-flow mixing)	Chevron STB (gas mixing)	Fluidized bed or cascading bed, fine solid particles, char fuel

in a manner similar to that used in the Tosco process. Mixing is provided by the fluidized bed and the falling balls.

• In the Lurgi process,¹⁶ hot burned shale is rapidly mixed with raw shale in a screw mixer and then held in a surge bin for a few minutes to complete the pyrolysis. After pyrolysis the shale is fed to a lift pipe (dilute fluid bed) where it is burned as it is pneumatically lifted upward in a stream of air. The hot burned shale exiting from the lift pipe provides a continuous source of hot solid.

• In the Chevron process,¹⁷ raw shale and hot burned shale are mixed in a fluidized bed and held there until pyrolysis is complete. Although a fluidized bed (a suspension of solid particles in a gas) provides good vertical mixing, the residence time of solids is not uniform. To correct this problem a number of stages are introduced into the fluid bed to provide a more uniform residence time. A lift pipe is used to burn retorted shale and provide hot solid as in the Lurgi process. The use of a lift pipe for burning shale in both of these processes (Lurgi and Chevron) limits the maximum particle size that can be processed to a diameter of about 0.5 cm.

• In the LLNL cascading bed process, mixing occurs in a few seconds as the solids--recycled burned shale and raw shale--flow down a series of chutes that invert and redirect the flow. Pyrolysis is completed in a few minutes as the hot shale particles flow through a bin. The char is burned to produce hot solid in a cascading bed burner rather than in a lift pipe. Solid particles cascade down a series of chutes which slow their fall and provide sufficient residence time for combustion. Oxygen is provided by air flow across the tumbling solid particles. The maximum particle size may be as large as 1 or 2 cm in diameter because the vertical pneumatic lift pipe used in this process is not restricted to the operating conditions required for char combustion.

ANALYSIS AND EVALUATION OF FOUR GENERIC RETORTING PROCESSES

Faced with this variety of retorting processes, we would like to be able to answer the question: Which one is the best? Although we are a long way from knowing the answer, we do know it will depend on the cost to produce shale oil from any given shale feed. None of these retorting processes has been operated on a commercial scale. Cost estimates are based on engi-

neering designs of widely varying detail and reliability. Some of the designs are very tentative, being based on concepts that have not yet been implemented, whereas others represent actual experience with large-scale pilot or semi-works plants. In no case has even a single full-scale module of a commercial retort been operated. An additional problem is that details of both the technology and the cost estimates are considered to be proprietary by most companies, and hence are not publicly available.

Although cost estimates, even comparative cost estimates, must be viewed skeptically, we believe that technical evaluations and comparisons of the generic processes are worthwhile and informative, even if complete technical operations data are not available. By this means, the state of the art may be more clearly defined, advantages and disadvantages of various processes may be identified, and opportunities for improving the present processes may become apparent. In the course of this analysis, we have developed a new process concept, the LLNL cascading bed process, which may offer advantages over the other processes evaluated.

We selected four generic retorting processes for evaluation, two hot-gas processes and two hot-solid processes (see Table 3):

• A moving-packed-bed retort with hot gas supplied by internal combustion. Example: the Paraho process.

• A moving-packed-bed retort with hot gas supplied by an external combustion heater. Example: the Union B process.

• A fluidized-bed retort with hot solid supplied by the combustion of retorted shale in a lift pipe (a dilute-phase fluid bed). Example: the Chevron staged-turbulent-bed (STB) process.

Table 3. Summary of the four generic oil-shale retorting processes selected for analysis and evaluation.

Process name	Abbreviation	Modeled example
Hot gas, internal combustion	HGIC	Paraho
Hot gas, external combustion	HGEC	Union B
Hot solid, fluid bed	HSFB	Chevron
Hot solid, cascading bed	HSCB	LLNL

● A gravity-mixed retort with hot solid supplied by a cascading bed burner. Example: the LLNL cascading bed process.

These retorting processes are not at an equal stage of development. The Paraho process has been operated at a semi-works scale, and engineering design has been prepared for scale-up to commercial size. The Union B process is under construction as the first full-scale module of a commercial plant and should begin operation this year. The Chevron process has been operated at a laboratory scale, and a pilot plant is under construction. The LLNL process concept is being tested in the laboratory.

Analysis and Evaluation Method

In order to make comparisons of the various generic processes, a detailed description of each process is required. The description must include the amount and rate of flow of all material—gas, solid, and liquid—entering and leaving each process component, and also the amount of energy entering and leaving each component. This requires knowledge of the chemical reactions occurring in each component, the pressure drops, and the energy needed to move material through the equipment.

We are somewhat hampered in making the comparisons by incomplete knowledge of the processes. On the one hand, the existing understanding of the generic processes is not always sufficient to provide us with the detailed description of each process that we need. On the other hand, not all the existing information on the proprietary processes is publicly available. Fortunately, the situation is not hopeless. Qualitative descriptions of many processes are publicly available, and we begin with these. Furthermore, a substantial understanding of the chemical and physical processes important in oil shale processing has been developed at LLNL and other laboratories in recent years.^{18,19} Mathematical models incorporating this understanding have been developed at LLNL, and we have used these models in constructing detailed descriptions of each process.^{20,21}

Each generic process model was constructed using the following information:

● LLNL mathematical models of the retorting process, based on kinetic and thermodynamic data for the relevant chemical reactions and physical processes.

● Our interpretation of qualitative information available about each proprietary process.

● Our designs for additional components where required.

● Our designs for process optimization suggested by model calculations. These changes improve the process without changing the concept.

For all four processes we have assumed a shale feed grade of 30 gal/ton and production of 50,000 barrels/day of crude shale oil (no upgrade) or the equivalent energy content of oil plus gas.

We believe that these models are suitable for evaluating and comparing the four generic processes. While it is convenient to list "proprietary" examples of each of the generic processes, these examples almost certainly differ from the generic processes described here. The differences, however, should not be large enough to affect the general evaluation and comparison of generic processes that we will make.

The model calculations allow us to construct flow sheets of mass and energy and to understand each generic process well enough to make some useful comparisons. The calculations are also helpful in identifying problem areas and research opportunities.

RGIC Process

The Paraho process was used as a starting point in modeling the hot gas, internal combustion (RGIC) process. In the Paraho process, raw shale is fed into the top of the retort and moves downward through it. About 15% of the raw shale is smaller than 1.2 cm in diameter and is rejected. Recycle gas is introduced at the bottom of the retort, and mixtures of air and recycle gas are introduced at an upper and a lower distributor within the retort. Combustion of recycle gas, char, and some oil vapor occurs above the two distributors, providing a supply of hot gas which heats and pyrolyzes the shale. The oil mist and vapor are transported to a condenser where oil is collected.

The LLNL model for a moving-packed-bed retort with hot gas supplied by internal combustion includes the chemical reactions and physical processes shown in Table 4. Model calculations have been validated by comparison with many laboratory experiments at LLNL and with data from Paraho retort runs. The excellent agreement between calculated and measured temperature in the Paraho semi-works retort (2.4 m diam, 8.2 m high) is illustrated in Fig. 3 for typical operating conditions. The calculated oil yield, gas composition, and spent shale composition also compare well with the experimental results.²²

Table 4. Mathematical model elements used in analyzing HGIC, HGEC, and HSCB processes.

Chemical reactions in shale particles:

- Release of bound water.
- Pyrolysis of kerogen and coking of oil.
- Pyrolysis of char.
- Decomposition of carbonate minerals.
- Reaction of carbon with carbon dioxide.
- Reaction of carbon with oxygen.
- Reaction of carbon with water.

Chemical reactions in gas stream:

- Combustion and cracking of oil.
- Combustion of H_2 , CH_4 , CH_x , and CO.
- Water-gas shift.

Physical processes:

- Axial convective transport of heat and mass.
- Axial dispersive transport of heat.
- Heat transfer between gas stream and shale particles.
- Thermal conduction within shale particles.
- Water evaporation and condensation.
- Movement of shale countercurrent to flow of gas.

Using the model to simulate a larger-scale retort (10 by 40 m in cross section and 8.2 m high), we found that some operating changes might be desirable. The predicted oil yield can be significantly improved by increasing the separation between the combustion zone and the retorting zone. This can be done by moving the air distributors 1 m downward and increasing the recycle gas flow into the bottom of the retort by 55%. The peak temperature is substantially higher than in the semi-works retort because of the lower heat loss

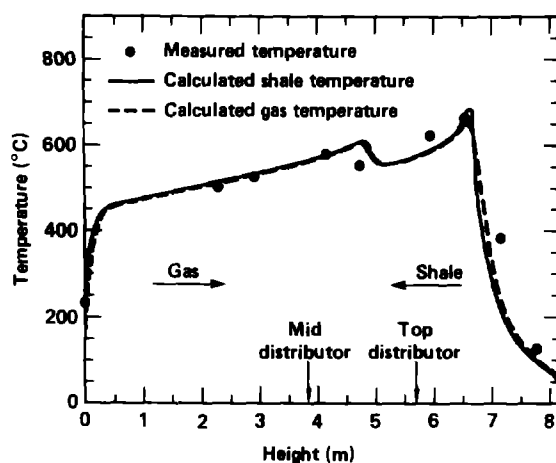


Fig. 3. Comparison of measured and calculated temperature profiles in a Paraho retort. The good agreement between the calculated and measured temperatures from the bottom of the retort (left) to the top (right) confirms and verifies our understanding of this retorting process.

from the surface and because the higher flow of recycle gas captures more of the sensible heat of the outlet shale. The peak temperature can be limited, however, by reducing the air flow by 35% at the top distributor. This change also reduces the outlet gas temperature, thereby reducing the heat load at the oil condenser. We assume that oil would be condensed from the outlet gas at 10°C in a commercial process, rather than at 60°C as in the semi-works plant. This would reduce the amount of oil vapor recycled with the gas and burned in the retort.

Mass flow in this HGIC process is shown in Fig. 4. The widths of the streams in the figure are proportional to the mass flowing in the process. The mass of the raw shale is reduced by pyrolysis of the kerogen, combustion of the char, and decomposition of the carbonate minerals. Inasmuch as most of the energy produced from burning char is absorbed in the decomposition of the carbonates, the fuel contained in the recycle gas is essential. The HGIC process is thermally efficient in that solids and gases enter and leave the retort at relatively low temperatures. Because the gas cycle is diluted by nitrogen from the introduced air, it may not be practical to utilize the fuel value of the gas outside the retort, and it is not practical to condense all the liquid product from the large volume of recycle gas.

HGEC Process

The Union B process was used as the starting point for the hot gas, external combustion (HGEC) model. In this process, shale is pushed upward through

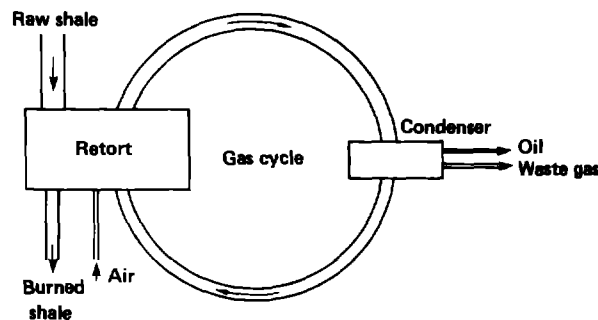


Fig. 4. Mass flow diagram for the HGIC process (hot gas, internal combustion). The relative masses flowing in the process are represented by the widths of the streams. The mass of gas flow required is almost as large as the mass of solid being processed. Shale leaving the retort is completely retorted, and one-fourth of the char produced has been burned. Product oil must be separated from a large mass of waste gas.

the retort by two alternating pistons. Gas heated in an external heater flows downward through the retort, and oil may be removed as vapor or mist, or may flow downward as a liquid. The LLNL moving-packed-bed model was used to simulate the HGEC process. The calculations are somewhat simplified compared with the HGIC process, because it is not necessary to consider oxidation reactions within the retort.

Only the approximately 6% of the shale feed material that is smaller than 3 mm is rejected. By choosing to process more of the finer shale particles than the Paraho process, the Union B process rejects less material but at the cost of higher resistance to the flow of hot gas. According to published information, the walls of the retort diverge upward to permit the shale to be pushed upward by the rock pump. The angle of this divergence has an important additional influence on the pressure drop through the retort. We calculated that, for a given cross section at the top of the retort, a 15° divergence from vertical walls would increase the pressure drop in the retort from 20 to 63 kPa (0.2 to 0.63 atm). For our HGEC model calculations, we assume a divergence of 10° and calculate a pressure drop of 40 kPa (0.4 atm). We recirculate the recycle gas directly to the heater at the calculated exit temperature of 94°C because our model results indicate that a negligible amount of the oil vapor in the gas would be lost to coking or cracking when recycled through the retort. The remaining gas stream is condensed at 10°C to remove product oil.

The recycle gas is heated by burning product gas and oil. For the assumed shale feed grade of 30 gal/ton, it is necessary to burn all of the product gas and 2.9% of the product oil. For a shale grade of 36 gal/ton, only 0.8% of the oil would have to be burned, whereas for a shale grade of 24 gal/ton, 6.1% of the oil would have to be burned.

The mass flow in this HGEC process is shown in Fig. 5. Use of an external heater offers some important advantages. It avoids dilution of the circulating gas with nitrogen from air, thus allowing collection of almost all the liquid and hydrocarbon gas, and it eliminates carbonate decomposition in the shale during processing. But the product gas and part of the product oil (or fuel from an external source) must be used to run the heater. In addition, the spent shale (with the char remaining on it, unused) exits at a much higher temperature than in the HGIC process, yielding a lower thermal efficiency.

HSFB Process

The starting point for our model of the hot solid, fluid bed (HSFB) concept was the Chevron STB process, in which raw shale is mixed with hot burned shale in a fluidized bed and retained in the bed until pyrolysis is essentially complete. To provide a uniform residence time for particles in the fluidized bed, stages are added to ensure that the mixture moves downward more or less uniformly. The mixture of retorted and partially burned shale is then introduced into a pneumatic lift pipe. As the particles are lifted in a column of air, the fuel (char) remaining on them is burned, raising their temperature. The heated solid material is separated from the gas stream at the top of the lift pipe, at which point some of it is discarded but a major fraction of it is mixed with new raw shale in the retort, completing the cycle.

Models were adapted to calculate the major processes in this retort, including fluidization of the solids, pressure drop, kerogen pyrolysis, and release of bound water. This allowed us to select reasonable operating conditions and calculate mass and energy flow in the retort. The lift pipe was also modeled, including combustion of char and sulfur, combustion of the pyrolysis products from fines blown out of the retort, decomposition of carbonates, pneumatic transport of solids, pressure drop, and particle attrition. The pneumatic transport of a mixture of particles of widely varying sizes is not well understood, and this reduces confidence in our lift pipe calculations. For example, the most optimistic interpretation of recent data could result in a 40% decrease in the required

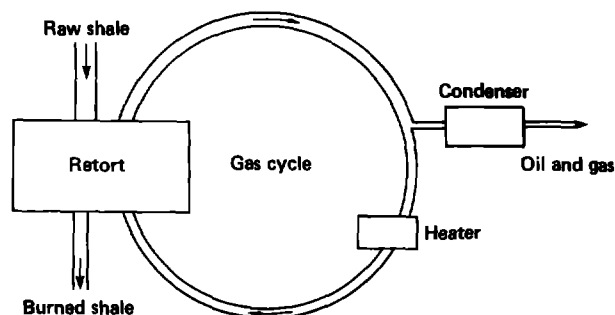


Fig. 5. Mass flow diagram for the HGEC process (hot gas, external combustion). The amount of gas required is comparable to the amount of solids processed. No air enters the retort, and the char is not burned. No waste gas is mixed with the product oil and gas.

height of the lift pipe.²³ It was also necessary to calculate the compression of gas streams, carbonate decomposition in a surge bin at the top of the retort, and heat exchange required in the process.

Figure 6 shows the mass flow in this HSFB process. The ratio of hot solids to raw shale is 3.5. The solids leave the retort at 500°C and are heated to 665°C in the lift pipe. Maximum particle size is 6 mm. Most of the shale (98%) is retorted, with a residence time in the retort of 3.6 min. The required height of the 8.4-m-diam lift pipe is 49.4 m, providing a residence time of about 11 s. The constraints of residence time and particle size make it difficult to reduce the height requirement without increasing the pressure. If it is economically practical to increase the pressure from 0.8 atm (ambient at the site) to 2 atm absolute, the height can be reduced to about 15 m. Another alternative may be to burn part or all of the char in a dense-phase fluidized bed.

Although more solids must be handled than in hot gas processes, the high throughput and relative ease of handling them in the HSFB process may be advantageous. Only a small amount of gas is required for fluidization, and both oil and hydrocarbon gas can be readily recovered. Char left on the retorted shale can provide all the energy required in the process.

HSCB Process

The hot solid, cascading bed (HSCB) concept was originated at LLNL. In modeling the hot solid pro-

cesses we came to realize that they might have some inherent advantages as compared to hot gas processes, especially in the relative ease of handling solids and in the efficiency of using char as fuel. Our reasoning was based on an analysis of the essential requirements of a hot solid process, which are:

- Rapid mixing of solids.
- Residence time of 2 to 5 minutes for pyrolysis.
- Rapid removal and cooling of the product to avoid cracking of oil vapor.
- Residence time of 10 to 20 seconds for the retorted shale in a combustor.

While the first and third conditions are easily met in a fluidized bed retort, the second condition is not. A fluidized bed provides mixing during the residence time, which is not only unnecessary but results in a nonuniform residence time. The Chevron process accepts the unnecessary mixing and attempts to make the residence time more uniform by introducing stages into the bed.

The lift pipe is an adequate way of lifting and burning shale, but the constraints are tight. The interrelationships between particle size, residence time, gas velocity, oxygen concentration, and combustion kinetics require a very high lift pipe and a small particle size. Moreover, control of a lift pipe during operation may be difficult.

We conceived our cascading bed process as a way of getting around these problems of the fluidized bed process (see Fig. 7). Raw shale from the feed supply

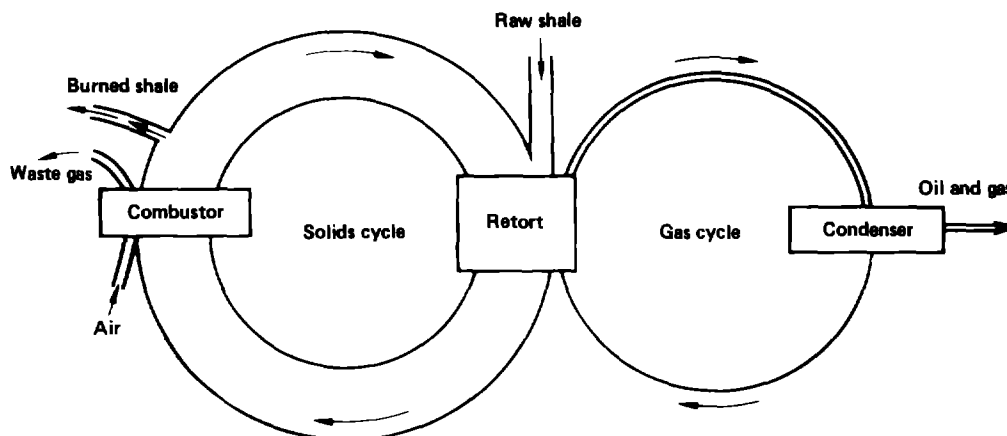


Fig. 6. Mass flow diagram for the HSFB process (hot solid, fluidized bed). A large mass of solid flow must be handled compared to the mass of raw shale processed. No waste gas is mixed with the product oil and gas. Char is efficiently burned to provide the heat for the process. (The mass flow diagram for the HSCB--i.e., hot solid, cascading bed--process is essentially the same.)

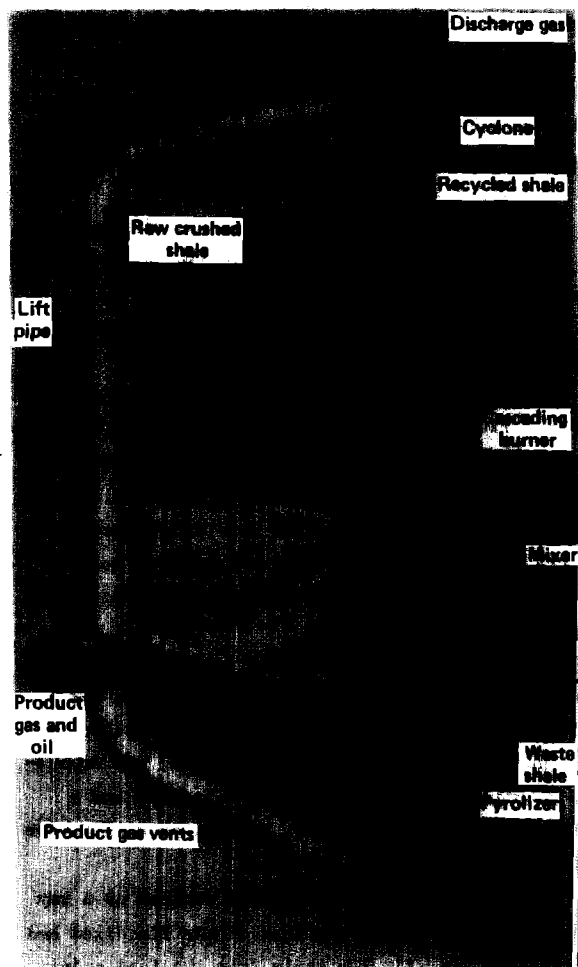


Fig. 7. Artist's rendering of a commercial-scale cascading bed retort. Raw crushed shale from the mine is mixed with hot burned shale from the cascading burner. The mixing occurs in a few seconds as the two streams of shale fall into the pyrolyzer. Gas and oil vapor products are evolved rapidly, especially at the top of the pyrolyzer, and are removed and cooled. Retorted shale at the bottom of the pyrolyzer is carried, first horizontally and then vertically, to the top of the retort by a blast of air. After air is removed in the cyclone separator, the shale flows down through the cascading burner; a lateral flow of air burns the char on the shale, raising its temperature. This hot shale is then mixed with more raw shale and the cycle is repeated.

and hot shale from the cascading burner enter the mixer, where they are rapidly mixed in an alternating series of chutes. The mixture flows into and through a pyrolyzer. Several minutes are allowed in the pyrolyzer to obtain complete pyrolysis of the kerogen. Gases and oil vapor are removed through vents in the pyrolyzer. The mixture of retorted and burned shale is then introduced into a short lift pipe whose only

purpose is to transport it to the top of the cascading burner (although some combustion inevitably occurs during this transport). The shale is separated from the gas at the top of the lift pipe and distributed into the top of a cascading burner, where alternating chutes retard its fall and provide the residence time required for full combustion. Temperature is controlled by adjusting the lateral flow of air across the burner, which is about 5 m high.

The computational model developed for the HGIC process was adapted to simulate both the retort and the cascading burner for the HSCB process; it includes all the chemical and physical processes listed in Table 4. In addition, the lift pipe model was used to calculate the small amount of combustion (about 25% of the total) that occurs during the pneumatic transport.

As a first step in developing this concept, we have built and successfully operated a laboratory-scale burner that measures about 4 m high and 8 by 15 cm in cross section (Fig. 8).

COMPARISON OF RETORTING PROCESSES

Many features of the four generic processes are presented for comparison in Fig. 9. Each retorting process is represented as a site containing the shale processing facilities required to produce 50,000 barrels per day of shale oil or its energy equivalent; for three of the four processes, an optional electric power generating plant is also included. The daily flow of materials in and out is shown on the same mass scale so that amounts may be compared. The unlabeled numbers are metric tons or megagrams (Mg) per day. In order to show the large masses of solid material (i.e., shale) on the same scale as other materials, we show them stacked ten units deep. Energy flow is shown in megawatts electrical.

The shale processing facility is shown by three columns representing the major components of the plants. The first is the volume of the reaction vessels required for handling the shale. For the hot gas processes, this is the volume of the retort itself. For the hot solid processes, it includes the pyrolysis vessels and the shale combustion vessels. Differences in the volume of this equipment should give qualitative ideas of capital cost differences for this portion of each process. The second column shows the heat exchange capacity for each process in megawatts divided by the log mean temperature difference, a number roughly proportional to the surface area required and

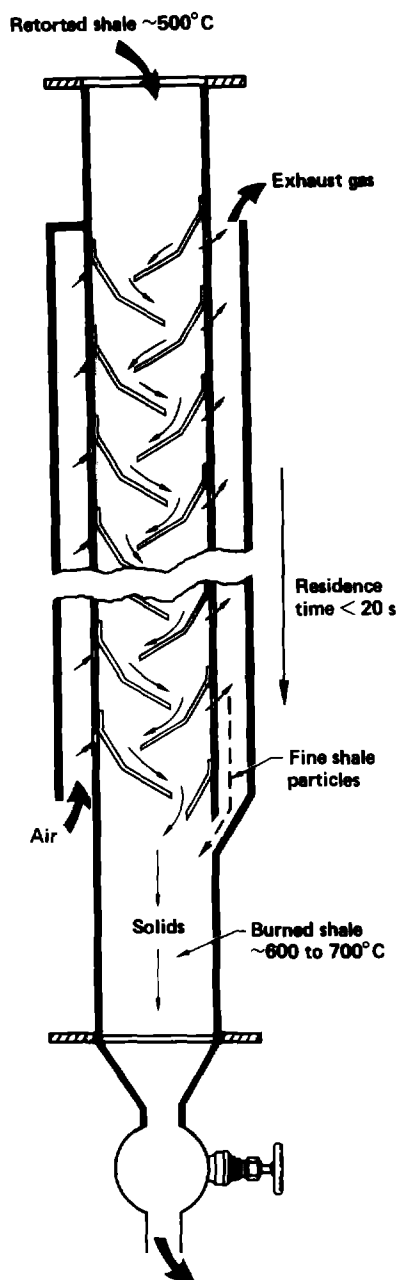


Fig. 8. Diagram of the cascading bed combustor. Air flowing from left to right burns the char on the shale as the fall of the shale is delayed by the chutes. The temperature in this combustor is controlled by adjusting the air flow.

also related to cost. The third column is the rotating machinery capacity in megawatts, which represents the electrical power requirement for the process plant.

Power plants to generate electricity from hot shale are optional in three of the processes (all ex-

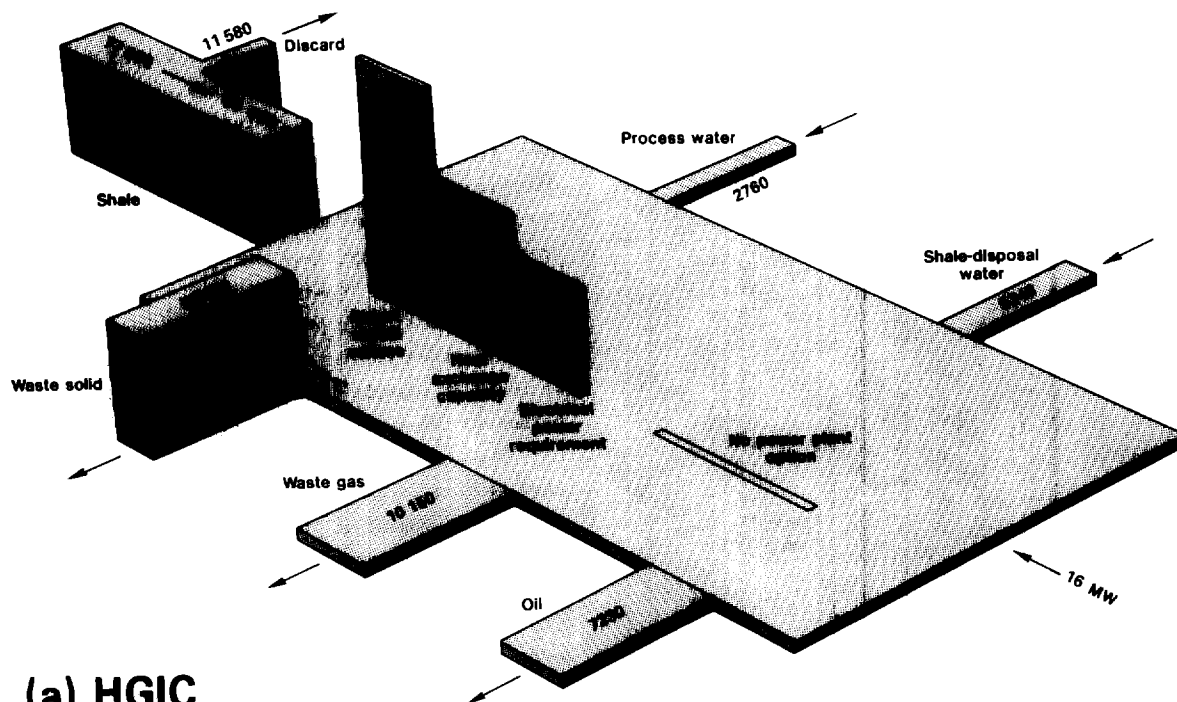
cept the HGIC process). Both heat exchange capacity and power generating capacity are shown for these.

In addition to the shale oil produced, hydrocarbon gas and hydrogen can be recovered in all the processes except the HGIC process. (In that process, most of the gas is used as fuel in the retort, and the rest is not worth recovering because it is diluted with nitrogen and combustion products.) The recovered gases may be sold after they are upgraded to pipeline quality, they may be used as fuel on site, or they may be used to make hydrogen. Hydrogen collected on site or produced from hydrocarbon gases will be needed to upgrade (hydrotreat) the shale oil. In the HGEC example in this paper, all the gas is burned in the external gas heater.

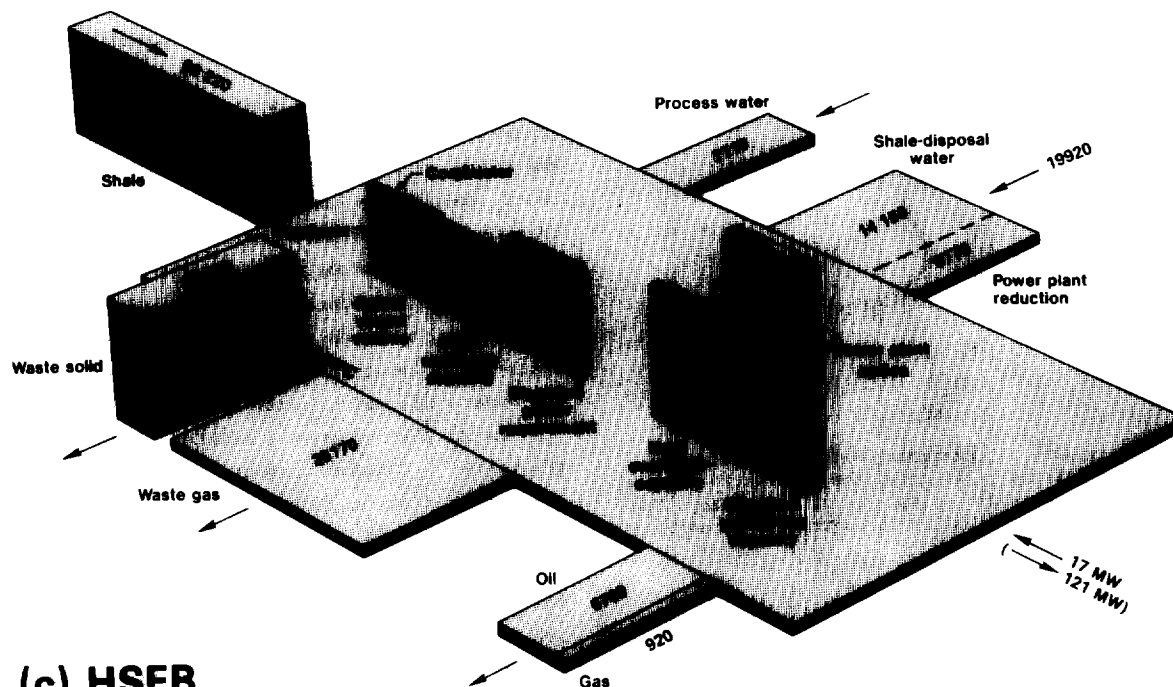
The two hot-solid processes use all the shale that is mined, whereas the two hot-gas processes must reject some amount of the finer shale particles. The HGIC process requires the largest mine because of the amount of fine particles rejected and the inability to recover the hydrocarbon gas and all the oil vapor. Although only a small amount of fine shale particles is rejected in the HGEC process, the total amount of mined shale is also substantially greater than that for the two hot-solid processes, because the hydrocarbon gas product and part of the oil product are used as fuel for the recycle gas heater.

The HGIC process requires the largest reaction vessel volume (9440 m^3), with a correspondingly large cross-sectional area (1157 m^2). In the HGEC process, the volume required (4300 m^3) is substantially reduced, even though less fine material is rejected. This is possible because combustion in the retort has been eliminated, along with the related control problems. Gas can therefore be moved through the retort much faster, although at the expense of higher pumping costs—as is apparent in the large machinery capacity and power requirement in the HGEC process.

In the HSFB process, a similar reduction in vessel volume is obtained without an increase in the pumping capacity and power required, even though a mass of solid 3.5 times as large as the raw shale input is being continuously recycled (see Fig. 6). The high efficiency with which solids can be processed in fluid beds makes this possible. Even so, a major fraction of the volume required (3760 m^3) is in the lift pipe combustor (2720 m^3). The height of the lift pipe combustor (about 50 m) and the difficulty in operating it with oil shale are problems that have yet to be overcome.



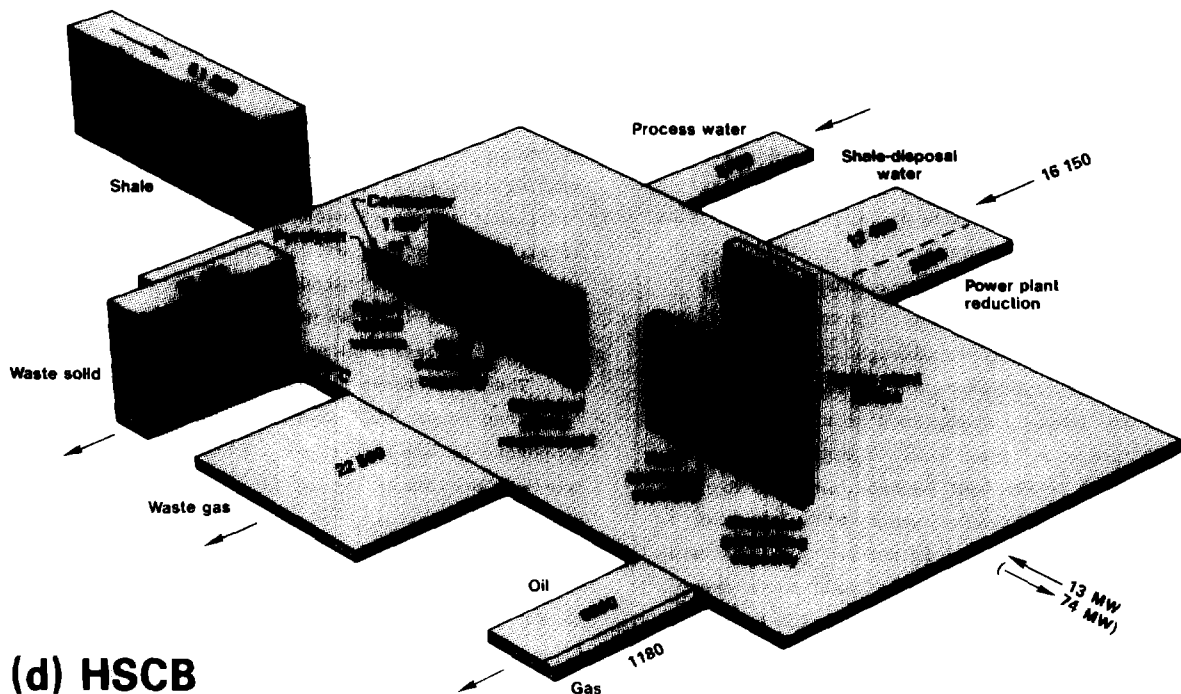
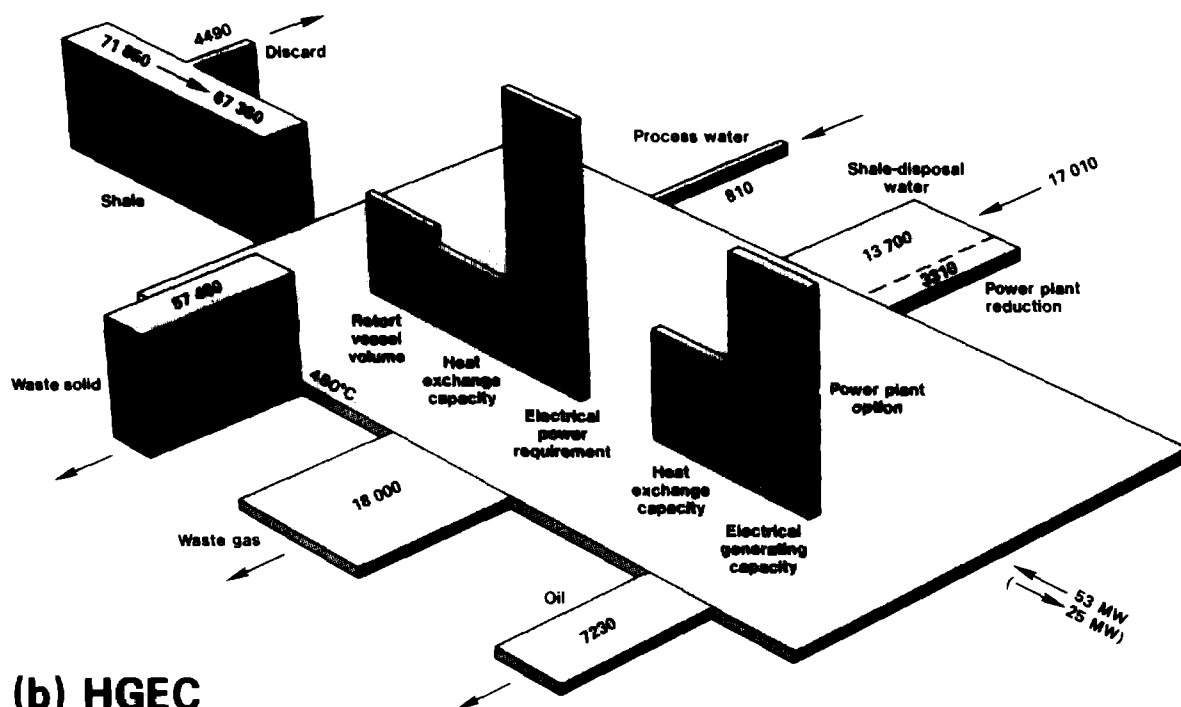
(a) HGIC



(c) HSFB

Fig. 9. The four generic retorting processes. (a) Hot gas, internal combustion (HGIC), e.g., Paraho process. (b) Hot gas, external combustion (HGEC), e.g., Union B process. (c) Hot solid, fluid bed (HSFB), e.g., Chevron

process. (d) Hot solid, cascading bed (HSCB), e.g., the LLNL concept. In these diagrams, the masses of materials entering and leaving a plant site are given by the numbers (in metric tons per day) and are shown to scale.



Energy flow in megawatts is shown, as is the net potential energy export from the site if the optional power-producing plants are provided. Major components of the retorting plants are shown, as are the compo-

nents of the optional power plants. Water required relative to oil produced is small for all four processes. Large volumes of solid materials must be handled in all these processes.

In the HSCB process, the vessel volume has been reduced to 1130 m³ by substituting a cascading bed combustor for a lift pipe, and a gravity-flow mixer and pyrolyzer for a fluidized bed. The mechanical equipment and electrical power requirements are slightly lower than those for the HGIC and HSFB processes. The problem in the HSCB process is to learn how to design and build a very large cascading bed combustor and mixer.

Cleanup of Waste Gases

In all these retorting processes, waste gas will be discharged into the atmosphere. Both the concentration of pollutants and the total amount of waste gas will have to be controlled to meet legislated levels. The waste gas from an HGIC retort contains large amounts of sulfur in the form of hydrogen sulfide and lesser amounts in other forms. It also contains hydrocarbons and some nitrogen compounds. Hydrogen sulfide must be removed, the gas must be oxidized, and additional sulfur in the form of sulfur dioxide may have to be removed. The cost of this cleanup processing will be an important part of the overall process cost. The hydrocarbon content of the waste gas is low, equivalent to approximately 100 Btu/scf (88 kJ/mol), but it may be practical to make power from the combustion of this gas. If so, the cost of gas cleanup may be reduced somewhat. The waste gas produced in the HGIC process (approximately 10,000 metric tons per day) will almost certainly be more difficult to clean than that from the other processes.

In the other three processes, the relatively small amount of gas from the pyrolyzer is not diluted with combustion products or nitrogen. Hence it may be used as a source of hydrogen for hydrogenation of the shale oil or cleaned and upgraded to pipeline quality. (Hydrogen from some source will be needed to upgrade the shale oil.) In the HGEC process, most of the gas is produced by combustion of whatever fuel is used in the gas heater. If the fuel is natural gas, the waste gas will be clean; if the fuel is coal, the cleanup equipment used in coal-burning plants will be needed. Use of a local fuel for the gas heater rather than an imported fuel is probably desirable. For example, burning char left on retorted shale would be preferable if it could be done economically, including the cost of cleanup of the waste gas.

In both hot-solid processes, large quantities of gas are produced by the combustion, in air, of char on retorted shale. In both processes, combustion occurs under conditions that seem to be advantageous for the

removal of sulfur from gas by reaction with the hot shale.

In general, nitrogen oxides in the gas are less important than the sulfur compounds, but they will require attention. In spite of the large amount of waste gas produced, the hot solid processes appear to have an advantage in requiring no cleanup of sulfur in the gas. The waste gas from the HGIC process may be the most expensive to clean, even though its volume is the least.

Water Requirement

Water required for each process is divided into two categories--process water and shale disposal water. The water needed for cooling at the oil condenser (for each process) and for cooling at the inlet air distributors (for the HGIC process) is shown in Fig. 9 as process water; the daily requirement is given in metric tons (or cubic metres). We note that the process water for the HSFB process is slightly greater than the amount of oil produced, while for the other three processes it is less than the amount of oil produced.

The temperature of the waste shale emerging from the process is shown in each diagram. In the HGIC process the temperature is relatively low (70°C) because of the high thermal efficiency. The water consumed in cooling this shale to ambient temperature, plus an additional amount of water equal to 10% of the mass of shale for wetting and compacting the waste shale and the unprocessed raw shale fines, is shown in Fig. 9 as the shale disposal water. It has been partially offset by the waste water produced from the retort.

The other three processes are not as thermally efficient as the HGIC process, hence the waste shale temperatures are much higher. The higher temperatures, however, provide an option for converting part of this energy to electricity before final cooling and wetting. The electrical generating capacity and the heat exchange capacity of the optional plants are shown, as is the water consumed in cooling and wetting the shale (i.e., for shale disposal), with and without the power plant. If a power plant is installed, there is a reduction in the amount of water consumed. Because the amount of water reduction is not economically significant, the question of whether to include the power plant will be determined by the cost of the plant and the value of the power. The power plant can make each of these three sites a net producer of electrical power.

CONCLUSION

In our opinion, no clear choice is apparent for a "best" process for large-scale, low-cost production of shale oil. Oil-shale process technology is neither highly developed nor mature, and substantial improvement can be expected from further research and development, and from industrial experience. The hot gas processes may be viewed as first-generation technology, and the hot-solid processes, if they can be successfully developed, may be second-generation technology.

Valuable engineering experience at the hundreds-of-tons-per-day scale has been obtained with the HGIC and HGEC processes, and the technology is moderately well developed for proceeding to the next step. The first module of an HGEC process plant (10,000 barrels per day) was completed in late 1983 by Union Oil Company, but initial operation has not yet occurred. The product gas will be cleaned up and burned as fuel in the first module. Later versions probably will use some less expensive fuel. Industrial operating experience with this process, supported by continued research and development, should make possible further improvements in efficiency and reductions in cost.

Scale-up of the HGIC process to commercial size may be a bigger technical risk than with the HGEC process, because of the difficulty of controlling the combustion process and flow of solid material in a large retort, and of cleaning up the waste gas.

The hot solid processes are not as highly developed as the hot gas processes, in many respects, because retort operating experience with these processes is limited to laboratory-scale operations or, on a larger scale, to short tests of some of the process components. Much information must yet be obtained on these hot-solid processes. In particular, we need to learn more about the important chemical reactions that take place during retorting. The hot solid processes, however, do offer the advantages of high throughput, low-sulfur waste gas, and reduced gas-pumping requirements. Potential difficulties center about our lack of experience in handling large quantities of fine shale particles in both the combustor and the pyrolyzer, and some uncertainty about oil cracking in the pyrolyzer.

The HSCB process offers several potential advantages over the HSFb process by substituting a mixer and gravity-flow pyrolyzer for the fluidized bed, and a cascading bed combustor for the lift pipe combustor. Elimination of the fluidized bed and of the need for controlled combustion in the lift pipe should permit the use of coarser material, reducing the amount of

fine material to be handled. At this stage of development, however, the HSFb process may have an advantage in scale-up because of industrial experience with fluidized beds comparable in size to that of the pyrolyzer. The larger lift pipe combustor, however, may prove more difficult to operate.

From our survey of these oil-shale retorting processes, it is evident that a balanced program of research and development in oil shale technology is needed, together with industrial development on an appropriate scale. This will lead to the technical advances that will make possible significant reductions in the cost of producing shale oil. Such an approach, however, will require the cooperation of government and industry in providing continuing support during the next decade.

Acknowledgment

This work was done under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

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